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PANEL ON FIRE RESEARCH AND SAFETY
MARCH 1-7, 2000**

VOLUME 1

Sheilda L. Bryner, Editor



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MATERIAL PERFORMANCE AND TESTING U.S. OVERVIEW

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ABSTRACT

This paper provides an overview of activities pertaining to material performance and testing in the United States since the previous UJNR panel meeting on fire research. The first part of this paper focuses on recent materials related fire research activities. The second part focuses on testing of marine products for regulatory compliance, and on increased uses of the Cone Calorimeter.

MATERIAL PERFORMANCE

Although halogenated flame retarded materials are not an environmental issue yet in the U.S., continued concern in Europe and Japan about the potential formation of dioxin from the incineration of their spent end products is influencing U.S. industry to seek alternative, non-halogenated flame retarded end products, in particular, for electronic components. A phosphorus based flame retardant approach is one of the most popular alternatives (metallic hydrates are others) but another new approaches are being explored. One of these is polymer-clay-nanocomposites which are polymers intercalated into the gallery spaces of layered nanosize silicate minerals to generate large interface areas between the silicates and the polymer. A reduction in heat release rate has been reported for various polymer resins with the use of appropriate organic treatments to compatibilize polymer resins and the silicate layers¹. The flame retardant effectiveness is indicated by the fact that the addition of a mere 0.1 mass % of organically treated montmorillonite to polystyrene reduces peak heat release rate by about 40%². However, the reduction in heat release rate tends not to be significant for further addition of clay beyond 3-5 mass %. It has been reported that the effect of the organic treatments on the clay surface on flammability properties of cyanate ester is complicated because one of four different treatments studied increased heat release rate over that of cyanate ester without any clay addition (the other three treatments significantly reduced heat release rate)³. Therefore, many studies are currently being conducted to determine the effects of the many parameters of clay-nanocomposites such as the type of clay, its organic treatment, intercalated vs. delaminated claylayers, molecular weight of polymer resin, and others on flammability properties. Another interesting, new FR approach is the enhanced formation of char to reduce heat release rate of polystyrene using Friedel-Crafts chemistry⁴. With the addition of a small amount (10%) of 2-

ethylhexyldiphenylphosphate to a copolymer of styrene and 4-vinylbenzyl alcohol (10%), evidence of char formation was observed and the peak heat release rate was reduced by 60%.

The feasibility of a new measurement technique using mid-infrared (MIR) transmitting fibers coupled to a Fourier transmission infrared (FTIR) spectrometer to monitor changes in the condensed phase spectra of burning polymers was demonstrated⁵. The measurement is used to investigate thermally induced changes in polymeric materials during their burning. The fiber optic set-up used in the experiments consisted of a sapphire probe (300 μm in diameter and 10 cm in length) which was mounted on a steel rod and connected at both ends to zirconium fluoride (ZrF) cables. A reflectance spectrum results from the attenuation of the evanescent wave due to absorption by the polymer (and its degradation products) in the immediate vicinity of the probe as shown in Figure 1. The spectra obtained early in the cone calorimeter experiment (*i.e.*, before ignition) and in the vicinity of the peak heat release rate are compared to a spectrum of nylon-6 measured using a diamond reflectance probe at room temperature. This type of measurement for the sample with a flame retardant additive would be extremely useful to understand the FR mechanism. However, such measurement is much more useful if the technique is extended over the wider infrared range instead of the current mid-infrared range.

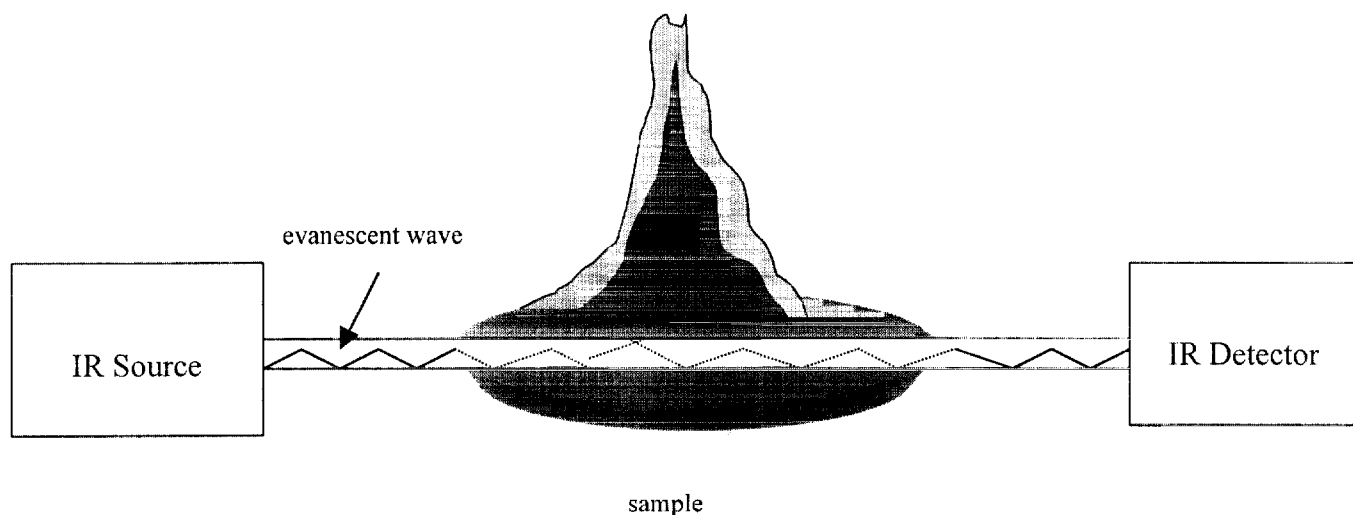


Figure 1. A schematic illustration of the real-time mid-infrared transmitting spectroscopic measurement of a sample during burning in the Cone Calorimeter.

An extensive materials fire research program has been conducted by Dr. Richard Lyon at the FAA Technology Center for application to fire safety of commercial aircraft interior materials. They have developed a unique device, a pyrolysis-combustion flow calorimeter (PCFC) to measure flammability parameters of milligram-sized research samples. This device consists of a high heating rate thermogravimetric analysis followed by complete oxidation of the degradation products with oxygen consumption measurement to calculate heat release rate. The validity of the measured heat release rate is demonstrated by the excellent correlation with those measured in the Cone Calorimeter as shown in Figure 2. This device is particularly useful for the

evaluation of new laboratory-produced polymers because the available amount of the experimental polymer is generally extremely limited. More detailed discussion of the device and the analysis is presented by Dr. Lyon in this meeting.

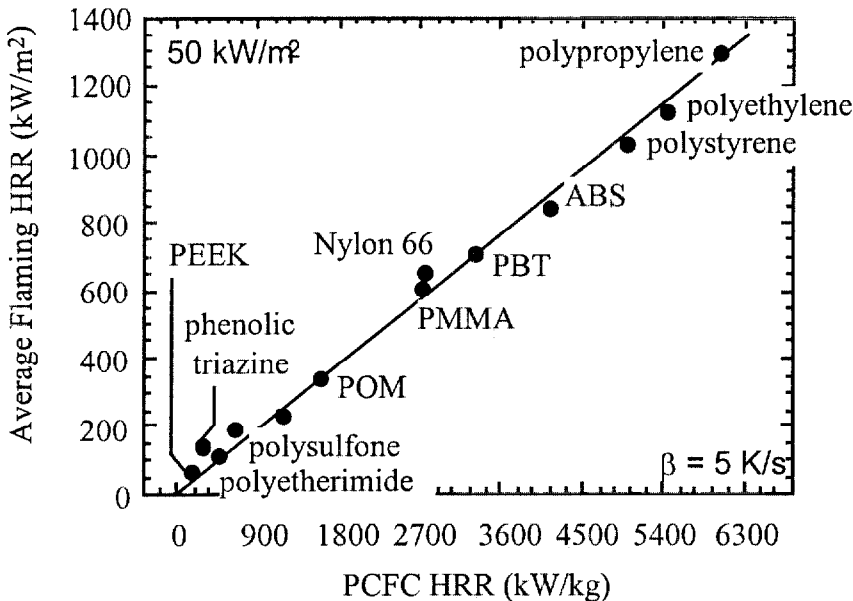


Figure 2. The relationship between heat release rate per unit mass measured in the Pyrolysis-Combustion-Flow-Calorimeter and average heat release rate per unit surface area measured in the Cone Calorimeter.

Another important, new research area, which has started recently at NIST, is a study of the effects of polymer melt flow on flammability properties of thermoplastics. When the heated surface is not horizontal (and in real applications it typically is not), the molten layer will have a tendency to flow downward; this can have a profound effect on the gasification and burning rate behavior since heat and, possibly, burning material are being transported. This phenomenon has been observed frequently in real fires but it has been almost completely ignored by the fire research community presumably because of its complexity. However, this is becoming more critical for understanding fire growth due to a significant increase in the daily use of thermoplastics, such as the commodity polymers. Dr. Ohlemiller presents his recent results in this meeting.

TESTING OF MARINE PRODUCTS

Since the 1998 UJNR panel meeting on fire research, testing and qualification requirements have changed considerably for materials and products that are used on ships that engage in international service. These requirements are specified in generic terms by the International Convention for Safety of Life at Sea (SOLAS). SOLAS is maintained by the International Maritime Organization (IMO), an agency within the United Nations that is headquartered in London, England.

Prior to July 1, 1998 each administration was permitted to implement the requirements using its own standard test methods and acceptance criteria. For example, the U.S. Coast Guard (USCG), which is the administration having jurisdiction (AHJ) in the United States, specified ASTM E 84 tunnel test criteria for interior finish materials. This test is widely used in North America, but not anywhere else in the world.

As of July 1, 1998 the IMO Fire Test Procedures Code (FTP Code) came into effect, and every administration throughout the world was required within six months to change its requirements and specify the universally accepted test procedures and acceptance criteria in the FTP Code. This had a very significant impact on material manufacturers and suppliers to the U.S. marine industry, because the old system was very different from and generally less stringent than that based on the FTP code. For example, interior finish materials are now regulated on the basis of the IMO surface flammability test, which is more severe than the ASTM E 84 test. In addition, interior finish materials may have to meet smoke and toxicity requirements that are very stringent as well.

Another important element of the new system is the requirement for manufacturers to participate in a follow-up program administered by a third party agency that is accredited by the administration to perform quality audits on a regular basis to ensure that the quality of a product is consistent. The follow-up requirement adds greatly to the cost of obtaining a type-approval certificate, and many manufacturers are reluctant to engage in a testing and follow-up program because of the expense.

The new rules have resulted in an increased activity of qualification testing for marine products. Some research is being conducted to improve products that met the old requirements, and that need to be upgraded to fulfill the new acceptance criteria. The use of intumescent coatings and wraps is often explored to address this problem.

INCREASED USE OF THE CONE CALORIMETER

On 1 January 1996, the High Speed Craft Code (HSC) entered into force as part of the Safety of Life at Sea (SOLAS) convention. This code deals with all aspects of the construction and operation of high speed craft. The most common type of ships that are regulated by the code are fast passenger and vehicle ferries that operate within 4 hours from the shore. The code permits that a high speed craft be constructed of combustible materials, provided certain fire performance criteria are met. Materials that meet these criteria are referred to as "fire restricting materials." The determination of fire restricting materials is based primarily on one of two tests. Bulkhead lining, and ceiling materials are tested using the ISO 9705 room corner test. Acceptance criteria for ISO 9705 are published in IMO resolution MSC.40(64) (MSC 64/22/Add.1, Annex 4). Furniture components (other than fabrics, upholstery, or bedding) and other components are tested using the ISO 5660 Cone Calorimeter. A research program was initiated by the USCG at SwRI in August of 1997. The primary objective of the program was to establish acceptance criteria to qualify materials as fire restricting based on performance in the Cone Calorimeter test ISO 5660. The proposed acceptance criteria that resulted from the research were presented at the

IMO Marine Safety Committee meeting in February of 1999, and were accepted in slightly modified form. Samples are tested in triplicate at a radiant heat flux of 50 kW/m² for a fixed duration of 20 min, in accordance with ISO 5660-1:1993 (time to ignition and heat release) and ASTM E 1354-97 (smoke production). The criteria for fire-restricting materials tested in the Cone Calorimeter are as follows:

- Time to ignition greater than 20 sec.
- Maximum 30-sec sliding average heat release rate does not exceed 60 kW/m².
- Total heat release does not exceed 20 MJ/m².
- Time average smoke production rate does not exceed 0.005 m²/sec.

These criteria are now enforced to qualify fire restricting materials for use as components of furniture and other contents. Since they are consistent with the criteria for interior finish materials, they also provide a screening tool for materials that have to meet the ISO 9705 criteria. This is the first major use and application of the Cone Calorimeter for regulatory purposes.

Another area where the Cone Calorimeter is now used for regulatory purposes is rail transportation. The 1999 Edition of NFPA 30 specifies Cone Calorimeter criteria for interior materials of passenger rail cars, that can be used in lieu of the traditional requirements based on ASTM E 162, ASTM E 662, and other older test methods.

In the spring of 1997, seven companies and industry associations from the U.S. and Canada decided to sponsor a Cone Calorimeter interlaboratory test program. Reproducibility and repeatability were determined for the scalar variables measured in the Cone Calorimeter according to the protocol developed by the Board for the Coordination of the Model Codes (BCMC). The protocol specifies that samples be tested in the horizontal orientation in triplicate at 75 kW/m² for a fixed test duration of 15 min. The purpose of the project was to assist the model building code organizations, NFPA and various other groups in the development of a system to determine degrees of combustibility of building materials. Three U.S. and one Canadian laboratory agreed to conduct tests on sixteen materials. The results of this round robin show that the Cone Calorimeter, following the BCMC protocol, can provide precision similar to that cited in the current Cone Calorimeter standards. The findings from the round robin were submitted to a Task Group in ASTM, which is currently developing a standard based on the procedure that was used. This effort is paving the way for potential adoption of the Cone Calorimeter by the Building Codes.

Finally, at Southwest Research Institute we are seeing an increased interest in the use of the Cone Calorimeter as a predictive tool for other (typically larger scale) fire test procedures, such as the ASTM E 84 tunnel test, the NFPA 265/UBC 8-2 room test, and most recently the French Epiradiateur test. Sometimes, Cone Calorimeter data are used in conjunction with fire modeling. Tests are often supplemented with supplemental toxic gas analysis, using FTIR spectroscopy.

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